

Distribution and elemental identification of efficiency-limiting metal impurities in multicrystalline silicon solar cells

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INTRODUCTION

Given the tumultuous recent events on the international stage, energy independence is now a vital national security issue for most nations in the world today. Simultaneously during the recent years, photovoltaics (PV), the conversion of sunlight into electricity, has evolved from the notion of an environmentally-friendly albeit hardly cost-competitive source of energy to a viable and cleaner alternative means of generating electricity. The improvement of materials and processes, fueled by intensive research over the past years, has contributed to the recent photovoltaics manufacturing boom that has witnessed a 20% per year growth rate.

Newer and more cost-competitive materials typically make use of faster and relatively dirtier production techniques that increase the amount of transition metal impurities and structural defects incorporated into the solar cell material. Transition metals introduce energy levels into the semiconductor bandgap of silicon, facilitating recombination of photogenerated charge carriers. As a result, industrial solar cells fabricated from more cost-effective multicrystalline silicon (mc-Si) materials are typically only 12-16% efficient (laboratory record 19.8% for a 1 cm² cell area), compared to efficiencies around 15-17% for industrial solar cells made of high quality single-crystalline Czochralski or float-zone wafers (laboratory record 24.7% for a 4 cm² cell area). Intensive work has been conducted over the previous year at the ALS to better understand the defects that limit the efficiency of low-cost solar cell materials, and to determine which methods effectively mitigate their deleterious effects.

DEVELOPMENT OF NEW EXPERIMENTAL TECHNIQUES

The x-ray fluorescence microprobe at beamline 10.3.1 has the unique capability of detecting metal precipitates as small as 40nm in diameter with a spot size (spatial resolution) of 1-2 square microns. A major challenge to researchers was the correlation of the presence of metal precipitates with solar cell device performance. This problem has been resolved with the development of the X-ray Beam Induced Current (XBIC) technique. The principle of XBIC is the following: the same x-rays that fluoresce the sample also excite electrons within the bulk, just like sunlight does during normal solar cell operation. When a sample is scanned before the x-ray at BL 10.3.1, two-dimensional maps of elemental impurity distributions and recombination activity are simultaneously acquired. In addition, the XBIC technique can also be directly correlated to other non-synchrotron-based techniques that quantitatively measure the local minority carrier diffusion length, a parameter used to determine absolute device efficiency. This allows a one-to-one correlation between transition metal precipitates and their absolute effect on solar cell device performance with micron-scale resolution.

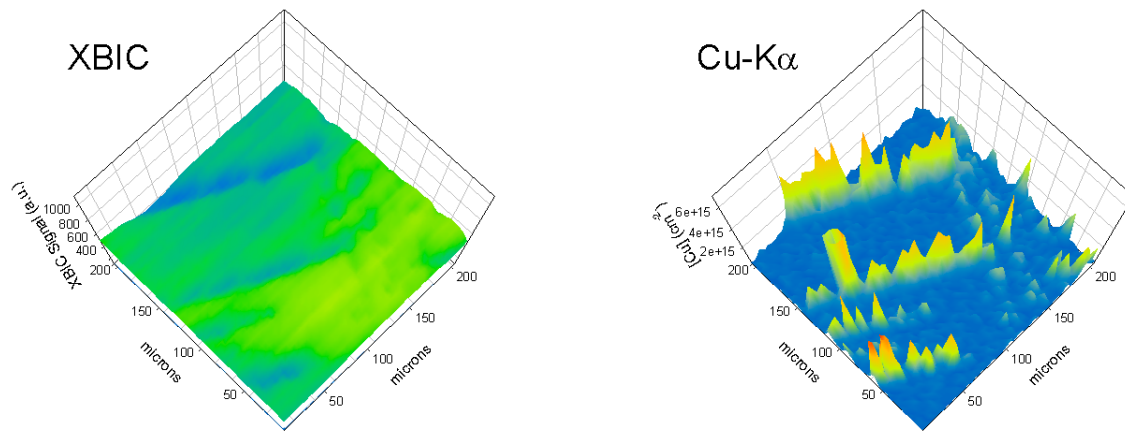


Figure 1. XBIC (left) and μ -XRF maps of the Cu-K α intensity distribution (right) of an area of a copper-doped Si-SiGe structure with misfit dislocations. Dark XBIC regions correspond to a reduction of the collected current whereas the bright Cu-K α regions correspond to increased copper concentration. An excellent correlation between the recombination activity and the copper concentration distribution is noted.

HYDROGEN PASSIVATION & METAL PRECIPITATION AT DISLOCATIONS

Model Si/Si_{0.98}Ge_{0.02}/Si structures, featuring a network of misfit dislocations, were used to study the precipitation behavior of metals at dislocations (a common crystallographic defect found in mc-Si). In addition, hydrogen passivation – a common technique used to reduce recombination activity in mc-Si – was tested on these samples. Cu- and Fe-doped samples were analyzed with XBIC/ μ -XRF before and after hydrogen passivation. The unpassivated Cu-doped samples showed a preference of Cu to form large precipitates at somewhat regular spacings along dislocations. Additionally, a comparison of the XBIC and μ -XRF data indicates a linear dependence of recombination activity on Cu concentration. This indicates that given the specific sample conditions, Cu precipitated in the form of platelets along the dislocations. For the unpassivated Fe-doped sample, the Fe distributed itself so homogeneously that the local concentration was below the detection limit for μ -XRF. The strong and uniform XBIC contrast along the dislocations suggests that Fe distributed itself homogeneously along the dislocation core, and possibly homogeneously within the bulk as well, although no large ($r \geq 20\text{nm}$) precipitates were formed. However, results were significantly different for the hydrogen passivated Fe-doped sample. In this sample, large electrically inactive Fe precipitates were observed near dislocation bunches, suggesting that hydrogenation may have played a role in the formation of electrically inactive precipitates, in effect redistributing the Fe within the sample. These previously unobserved effects warrant further study to fully comprehend the mechanisms involved in hydrogen passivation and metal precipitation.

METAL DISTRIBUTION IN INDUSTRIAL MC-Si

Commercially available Astropower thin sheet solar cell material was analyzed via μ -XRF/XBIC to determine how transition metals are distributed after aluminum gettering, a technique commonly employed to reduce the transition metal content in fully-processed solar cells. It was found that many metals remained within the solar cell material and were resistant to aluminum gettering. Iron was detected at grain boundaries and within intragranular structural defects that TEM analyses have identified as voids. Copper was co-precipitated with iron in the vicinity of a

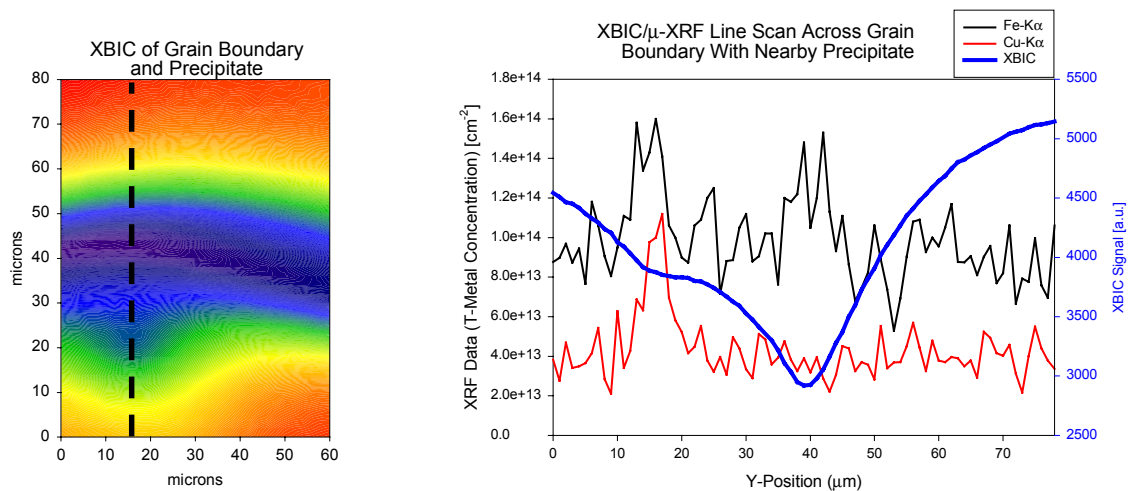


Figure 2. A 2-D XBIC map (left) shows a bulge appearing near a grain boundary in an industrial solar cell material. Dark XBIC regions correspond to a reduction of the collected current, representing an area of lower solar cell efficiency. A μ -XRF line scan (right) reveals this bulge is a precipitate composed of iron (black) and copper (red). In addition, iron is detected within the grain boundary, coinciding with the XBIC (blue) minimum.

grain boundary. In all cases, the local recombination activity increased – reducing the local solar cell efficiency – in the vicinity of these metals. Neutron activation analysis on this material confirmed that large concentrations of iron – on the order of 10^{16} cm^{-3} – remain after aluminum gettering. However, the precipitation of iron is not necessarily a bad thing for this solar cell material. If all this iron were not present in precipitates, but homogeneously dissolved within the bulk as iron-boron pairs or interstitially, the diffusion length (the average distance an electron travels before it recombines) would be reduced by at least a factor of 100. Since not all transition metals can be gettered, the challenge is to accumulate transition metals in localized regions of the solar cell in a chemical form that will be least detrimental to device performance. Future studies at the ALS will be dedicated to identifying the chemical state of the most dangerous impurities within solar cell materials. Improving our understanding of the chemical state and spatial distribution of transition metals in solar cells will allow us to better control the recombination activity of defects and to improve the efficiencies of low-cost solar cells.

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